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MAGNETIC ANISOTROPY OF MOLYBDENITE AT DIFFERENT TEMPERATURES

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ABSTRACT. The diamagnetic anisotropy and one of the principal susceptibilities of molybdenite crystals have been measured from 700° K down to 80° K. At low temperatures, the anisotropy tends to become independent of the temperature and at high temperatures its variation tends to obey approximately the Curie law. From the nature of the variation of the anisotropy with temperature and the considerations of its structure, the presence of metallic electrons having their motions restricted along the basal plane has been concluded. An attempt has been made to study the behaviour of these electrons in the light of modern theoretical investigations.

INTRODUCTION

Molybdenite crystal belongs to the hexagonal system and occurs in the form of a thin flake parallel to the basal plane. From the consideration of its structure it has been decided (Hultgren, 1932) that the binding between the molybdenum and sulphur atoms in it are essentially of the co-valent type; but the exact nature of the bonds that are formed along the basal plane is difficult to ascertain. The interatomic distances observed along that plane do not support the presence of ionic bindings. Workers on stereo-chemistry however, suggest the presence of bonds of partially metallic character. This view receives further support from its metallic lustre along the cleavage planes, metallic reflection from its surface (0001) (Coblentz and Kahler, 1919-20) and from its appreciable electrical conductivity along this plane. Moreover, molybdenite being a semiconductor the presence of free electrons in it does not appear improbable. The presence of free electrons having their mobility restricted along a plane should cause an enhanced amount of diamagnetism at right angles to that plane.

The magnetic measurements on molybdenite single crystals (1944) showed that whereas its susceptibility along directions in the basal plane, χ_1, has the value -44.3×10^{-6} per gram. mol., the susceptibility along the hexagonal axis, $\chi_{\parallel}$, is about -87.1×10^{-6} per gram. mol. *i.e.*, the anisotropy is about 72 per cent. Thus our above conjecture receives much support from this finding. Now it seems proper to extend these measurements to various other temperatures, both high and low, since it is known that the free-electron-susceptibility is extremely temperature sensitive. The present paper gives an account of these measurements.*

EXPERIMENTAL

Since the difference between the two susceptibilities is easier to measure accurately than either of them separately, measurements have been made of the anisotropy $\chi_1 - \chi_{\parallel}$, and of the smaller of the two susceptibilities χ_1, at different temperatures.

* A preliminary report of these measurements was published in *Nature*, **156**, 240, 1945.

(i) Measurements of Anisotropy at Low Temperatures :

Before describing the actual measurements at low temperatures a brief description of the cryostatic arrangement for attaining any desired temperature between room temperature and 80° K will be given. The arrangement is quite similar to that designed in this laboratory by Dr. A. Bose (1940). It is of the gas flow type. The flow chamber of the cryostat is a cylindrical double-walled copper vessel closed at both ends. It is made of thin sheet of copper and is kept inside a cylindrical Dewar vessel. The gas flow chamber contains a large number of thin copper discs perforated by small holes, the planes of the discs being at right angles to the axis of the cylinder. The discs are arranged in such a way that the holes in the consecutive discs are not in a line, so that the flow of the gas is turbulent and hence a thorough interchange of heat between the gas and the cryostat is obtained. The large mass of copper employed ensures a steady temperature, and due to large conductivity of copper there is very little temperature gradient. Through a hole along the axis of the disc is inserted a thin walled copper tube in which is kept the specimen whose properties are being studied. The space between the double walls of the copper chamber is connected to a mercury manometer and constitutes a constant volume air thermometer. Any change in the volume of air in this chamber due to temperature change in the cryostat operates a sensitive relay which controls the pump supplying the cold air flowing through the cryostat. In actual practice, liquid air is sucked at an adjustable rate directly into the cryostat and the desired temperature kept steady within 0.1°C may be obtained.

The measurements of the magnetic anisotropy were made by the usual torsional method. The crystal is suspended inside the copper tube of the cryostat, with its basal plane vertical. The suspension for the crystal consists of two parts. The upper part is a fine quartz fibre, which has been calibrated previously and the lower part is a thick glass fibre, sufficiently stout in comparision with the quartz fibre to be regarded as rigid. The whole length of the quartz fibre is above the cryostat, and is practically at room temperature all the time, so that its torsional constant is independent of the temperature of the cryostat. The whole cryostatic arrangement is placed between the flat pole pieces of a large electro-magnet, so that the crystal remains in the centre of the field. The upper end of the quartz fibre is attached centrally to the pin of a graduated torsion head. The torsion-head is initially adjusted so that when the crystal takes up its natural orientation in the magnetic field, namely with its basal plane along the field, the torsion of the fibre is zero. If the torsion head is now slowly rotated from this position there will come a stage when the equilibrium of the crystal in the field becomes unstable and the crystal suddenly turns. The field strength and the dimensions of the fibre have been so adjusted that α_c, the total angle by which the torsion head has been rotated from its initial position, is always more than 3 or 4 rotations of the torsion head. The anisotropy $\chi_{\perp}-\chi_{\parallel}$ per gm. mol. will then be given by the approximate relation :

$$\chi_1 - \chi_u = \frac{2M}{m} \cdot \frac{C}{H^2} \cdot \left(\alpha_c - \pi/4\right) \qquad \ldots \quad (1)$$

where m and M are the mass and molecular weight of the crystal respectively, H is the field strength and C is the torsional constant of the fibre.

The temperature of the cryostat is measured with a copper constantan thermo-couple, one junction of which is inside the crystal chamber, just below the crystal, and the other is kept at the temperature of melting ice. The thermo-couple is calibrated by keeping the latter junction at the temperature of melting ice and the former junction at four different temperatures covering the range within which the magnetic measurements are to be made.

(ii) Measurements of Anisotropy at high Temperatures

For the high temperature measurements the crystal is suspended inside a large-sized tube of unglazed porcelain, closely wound on the outside with "nichrome" wire, over which is rolled tightly a thin sheet of asbestos. By sending a steady electric current through the wire, the temperature inside can be maintained at any desired value up to about 800°C. Over the layer of asbestos there are a number of sheets of mica and over which there is an outer jacket for the circulation of cold water. The arrangement of water-circulation is for protecting the pole-pieces of the electromagnet from the influence of the high temperature. The temperature inside the chamber is maintained fairly steady.

The temperature is measured by a copper constantan thermo-couple, one junction of which is introduced inside the heating chamber through its bottom and is kept just below the crystal, while the other junction is at the temperature of the melting ice. The thermo-couple is calibrated as before by keeping the latter junction at 0°C and the former successively at four different steady temperatures covering the range of temperature required for this investigation.

The suspension of the crystal consists of two parts; the upper one is a fine quartz fibre as before which has been kept at the room temperature by means of water circulation; the lower one is now a thin copper wire to the lower end of which is tied rigidly the crystal with its basal plane vertical. The copper wire stands the high temperature better than the stout glass fibre used in low temperature measurements, and the use of cements for attaching the crystal is also thus avoided. The wire does not show any anisotropy. The method of measurements are the same as in the case of low temperature.

(iii) Measurement of χ_1

In view of the small value of χ_1, and its sensitiveness to small traces of impurities which are usually present in natural crystal of molydenite, and the uncertain temperature variation of the disturbing effect of the impurities, much

accuracy on the measurements of $\chi_\perp$ cannot be claimed. The measurements of $\chi_\parallel$ were made by the quartz torsion balance deviced by Dr. A. Bose for his measurements on paramagnetic crystals. It consists of quartz fibre stretched horizontally between a graduated torsion-head and a metal chuck. At the middle of this fibre is attached a light glass blance-beam at right angles to the fibre. A small vertical mirror is attached just over the mid-point of the beam. Any displacement of the beam can be observed from the mirror by lamp and scale arrangement. A small mica damping vane has also been attached to the beam. From one end of the beam is suspended the crystal system. The lower portion of the suspension consists of a stout glass fibre in low temperature measurements and a copper wire in case of high temperature measurements, the central portion is of quartz fibre and the upper portion a small length of a glass rod, the upper end of which has been bent into the form of a hook so that the whole system can be suepended from the balance beam. In the present measurements the suspension system has been attached rigidly with the balance beam by means of shellac. The length of the suspension system is so adjusted that the crystal which has been attached to the glass rod or the copper wire with basal plane vertical always remains within the cryostat or the heating chamber, in a non-homogeneous magnetic field—the gradient being in a vertical direction. Small aluminium and copper riders are placed at the other end of the beam until the beam becomes horizontal. When the field is switched on the crystal after taking up its natural setting position will move vertically along the gradient of the field. The resulting displacement of the beam can be very accurately observed by the lamp and scale arrangement. By rotating the torsion head, the beam and with it the crystal can be brought back to their original positions. The angle of torsion necessary for this purpose is evidently proportional to the susceptibility of the crystal. The room temperature value of the susceptibility being previously known, the values at any other temperatures can be extrapolated by simply observing the angle of torsion necessary at that temperature to bring the crystal back to its original position.

RESULTS

The results of these measurements are shown in Table I and II. These values are the mean of a number of observations taken with crystals from different specimens. The magnetic susceptibilities are expressed in E.M.C.G.S. units. From the tables it is evident that while $\chi_\perp - \chi_\parallel$, the magnetic anisotropy changes considerably from the highest to the lowest temperature, the variation of $\chi_\perp$, the susceptibility perpendicular to the principal axis, within the same range of temperature is extremely slow. These results are shown diagrametically in Fig. I.

TABLE I

T°K	$(\chi_\perp - \chi_\parallel) \times 10^6$ per gram mol.	T°K	$(\chi_\perp - \chi_\parallel) \times 10^6$ per gram mol.
90	46.4	255.5	43
113	45.4	298	42.7
127	44.8	334	41.6
146	44.5	384	40.8
160	44.3	462	40.3
172.6	44.2	482	40
190	44	566	39.4
229	43.4	730	36.8

TABLE II

T°K	$-\chi_\perp \times 10^6$ per gram mol.	TK°	$-\chi_\parallel \times 10^6$ per gram mol.
90	45	384	44
183	44.6	462	43.8
306	44.4	570	43.4

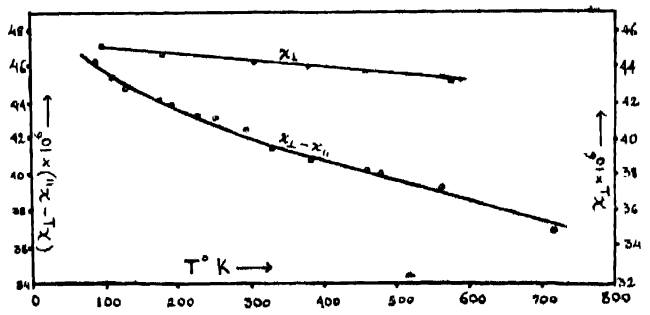

FIG. 1

CONSIDERATION OF THE STRUCTURE OF MOLYBDENITE

Molybdenite is a hexagonal crystal, with perfect basal cleavage. The molybdenum and sulphur atoms in it are arranged in parallel layers, each layer of molydenum atoms being sandwitched between two layers of sulphur atoms and these three layers form a composite layer by the repetition of which the whole structure is built. The various interatomic distances are represented as follows

Mo – Mo = 3.15 A.U. S – S = 3.15 A.U. Mo – S = 2.41 A.U.

and the distance between the two composite parallel layers of molybdenite has been found to be 3.66 A.U. The large distance between the adjacent layers shows that the binding between them is extremely loose and is probably of the Van der Waals type. The binding between M_0 and S has been proved to be of the covalent type (Hultgren, *loc. cit.*). But the bindings along the directions parallel to the basal plane seem to be of a partially metallic character. This view is supported by the metallic lustre of the cleavage face, appreciable electrical conductivity along directions parallel to the basal plane and the metallic reflection from its surface (*loc. cit.*). The interatomic distances along the basal plane also lends support to this view. The presence of metallic binding along directions in the basal plane postulates the existence of a free election gas having the motion of the electrons restricted along planes perpendicular to the hexagonal axis of the crystal. Consequently we should expect a temperature sensitive diamagnetic contribution perpendicular to the basal plane.

The diamagnetic properties of this crystal has recently been studied in this laboratory (1944). The susceptibility per gram molecule of the crystal perpendicular to the hexagonal axis, $\chi_\perp$, is about -44.3×10^{-6}. On the other hand, the susceptibility along the hexagonal axis, $\chi_\parallel$, is about -87.1×10^{-6}, *i.e.*, the anisotropy is about 72 per cent. Thus the diamagnetic anisotropy is directed along the hexagonal axis of the crystals. The numerical value of the anisotropy, which may be taken to be equal to $\chi_\parallel - \chi_\perp$, and which will be denoted by χ_e, appears to be the contribution from the mobile electrons in molybdenite, having their mobility restricted along the basal plane only.

TEMPERATURE VARIATION OF THE ANISOTROPY

The values of $(\chi_\parallel - \chi_\perp)$ per gm. mol. of molybdenite at different temperatures have been plotted against the reciprocal of the temperature in Fig. 2.

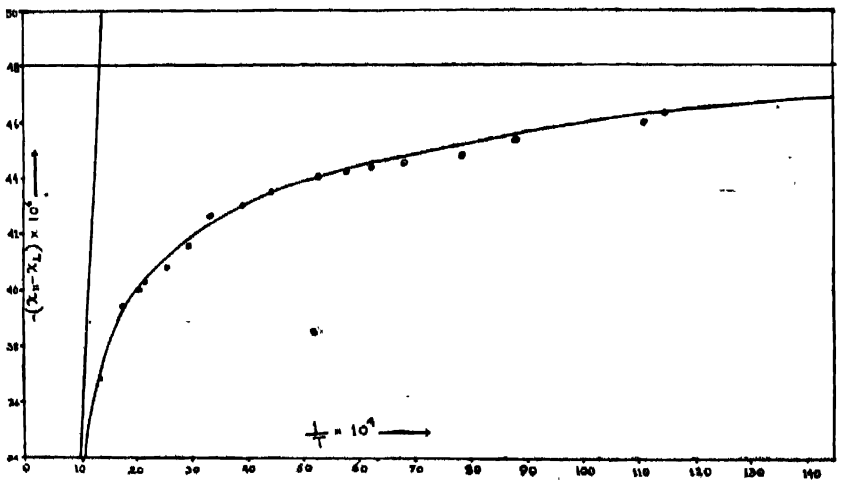

FIG. 2

It is observed that at low temperatures, the anisotropy tends to reach the temperature independent value of -48×10^{-6} per gm. mol. and at high temperatures it tends to reach asymptotically the value $\chi_e = \chi_\parallel - \chi_\perp = -\frac{.036}{T}$. From the nature of variation of the anisotropy with temperature, it seems that the magnetic anisotropy in molybdenite is a diamagnetic contribution from the free-electrons that might be present in it. Consequently it seems worthwhile to study the behaviour of these electrons in detail after the method developed by Ganguly and Krishnan (1941) in their investigations of the diamagnetic susceptibilities of graphite.

FREE ELECTRON SUSCEPTIBILITY IN MOLYBDENITE

Landau has shown that free-electrons should have besides their spin paramagnetism an appreciable amount of diamagnetism also and the numerical value of the diamagnetic susceptibility should be one third that of the paramagnetic one. At a temperatures very much lower than the degeneracy temperature, T_0, the diamagnetic susceptibility $(\chi_e)_d$ is given by

$$(\chi_e)_d = -\frac{n N \mu^2}{2kT_0} \quad \text{per gram atom} \qquad \ldots \quad (2)$$

And at a temperature $T^\circ >> T_0$

$$(\chi_e)_d = -\frac{n N \mu^2}{3kT} \quad \text{per gram atom} \qquad \ldots \quad (3)$$

where n is the number of free electrons per atom, N, the Avoradro number and the rest of the symbols have their usual significance. Stoner (1935) has further shown that when $T << T_0$

$$(\chi)_e)_d = -16.1\left(\frac{n}{V_0}\right)\left\{1 - 6.11 \times 10^{-9}\left(\frac{T}{V_0}\right)^2\right\} \text{ per gram atom} \qquad \ldots \quad (4)$$

and when $T >> T_0$

$$(\chi_e)_d = -\frac{124n}{T}\left\{1 - 3.23 \times 10^{-5}\left(\frac{V_0}{T}\right)^{\frac{3}{2}}\right\} \text{ per gram atom} \qquad \ldots \quad (5)$$

where V_0 is the maximum kinetic energy of the electrons in the completely degenerate state.

Now from fig. 2, it is seen that at very high temperatures the susceptibility $\chi_e = \chi_\parallel - \chi_\perp$ tends to reach asymptotically the value

$$\chi_e = -\frac{.036}{T} \text{ per gram mol.}$$

But from (3) $\quad (\chi_e)_d = -\frac{n N \mu^2}{3kT} = -\frac{.12n}{T}$ per gram atom.

Comparing these two relations we find n to be equal to 0.3. Taking MoS_2 to be a complex atom, this means that, 0·3 electrons are free per MoS_2 atom. Also considering (4) we still get n to be equal to 0.3.

Again from fig. 2 we find that at low temperatures χ_e tends to reach the temperature independent value of -48×10^{-6} per gram molecule. Thus from (2), n and $(\chi_e)_d$ being known, T_0 comes out to be about 1100°K. From these observations it can be said that the observed electronic susceptibility of molybdenite is the same as the susceptibility of a free-electron gas having an electron density of 0.3 per atom and a degeneracy temperature of about 1100°K. The full line curve in fig. 3 is the theoretical curve of such an electron gas drawn according to the Stoner's Equation (*loc. cit.*). The straight line represents the line $(\chi_e)_d=-\frac{n\mathrm{N}\mu^2}{3kT}$, which the theoretical curve tends to reach at high temperatures. It will be seen that the experimental values represented by circles lie close to the curve.

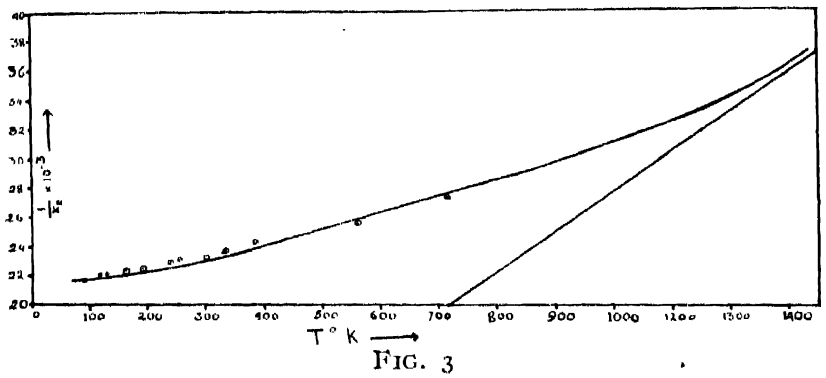

FIG. 3

In the above discussions no account has been taken of the effect due to the lattice field, which is generally very difficult, except, for the case dealt by Mott and Jones (1936), *i.e.*, when the surfaces of constant energy in K-space form a family of similar ellipsoids. For the present case, we shall proceed in a similar fashion, taking the magnetic field to be along the Z-axis of the energy ellipsoid. The diamagnetic susceptibility along the Z-axis may then be expressed as follows:

at high temperatures, $T>>T_0$

$$(\chi_e)'_d=-\frac{n\mathrm{N}\mu^2}{3kT}\alpha_1\alpha_2 \text{ per gram atom} \qquad (6)$$

and at low temperatures $T<<T_0$

$$(\chi_e)'_d=-\frac{n\mathrm{N}\mu^2}{2kT_0}\left(\frac{\alpha_1^2\alpha_2^2}{\alpha_3}\right)^{\frac{1}{2}} \text{per gram atom} \qquad (7)$$

where α_1, α_2 represent the ratio of the actual to effective mass of the electrons for motion along the x-y plane and α_3 that for motion in the perpendicular directions. Now, comparing (6) with the actual relation which the susceptibilities satisfy at high temperatures *i.e.* comparing.

$$(\chi_e)'_d=\frac{n.12}{}\alpha_1\alpha_2 \text{ with } \chi_e=-\frac{.036}{T}$$

we get

$$n\alpha_1\alpha_2=0.3 \qquad \ldots (8)$$

In view of the conclusion already obtained, the obvious solution that we get is

$$\alpha_1 = \alpha_2 = 1 \qquad \ldots \quad (9)$$

If we now calculate the degeneracy temperature of a free electron gas having 0.3 electrons per atom which has not been influenced by the effect of the lattice field, according to the usual relation

$$T_0 = \frac{\zeta_0}{k} = \frac{h^2}{2mk}\left(\frac{3n'}{8\pi}\right)^{\frac{2}{3}} \qquad (10)$$

where the various symbols have their usual significance, we get $T_0 = 14000°K$ approximately. But the degeneracy temperature which has been observed actually is about 1100°K. It is however known that the effect of the lattice field is to change the degeneracy temperature as follows

$$T'_0 = T_0(\alpha_1\alpha_3\alpha_2)^{\frac{1}{3}} \qquad \ldots \quad (11)$$

where T'_0 is the degeneracy temperature under the influence of the lattice field and T_0 that without the field. Thus we have

$$1100 = 14000\ (\alpha_1\alpha_2\alpha_3)^{\frac{1}{3}}$$

since $$\alpha_1\alpha_2 = 1$$

we have $$\frac{\alpha_1\alpha_2}{\alpha_3} = (13)^3 \qquad \ldots \quad (12)$$

which indicates a high eccentricity for the ellipsoidal surfaces of constant energy in K-space, being much elongated in directions perpendicular to the C-axis, their common axis being along the C-axis of the crystal.

Thus from the above considerations we see that the effective mass of the electrons for motion at right angles to the basal plane is enormous while that along the basal plane is just the actual mass. All these findings point to the fact that the mobility of these electrons is effectively restricted only in planes parallel to the basal surface.

DIAMAGNETIC ANISOTROPY IN MOLYBDENITE—A CONTRIBUTION FROM THE 'OVER-LAPPING' ELECTRONS

If we now consider the nature of the Brillouin zone for this structure we find that there is a *Zone* which can accommodate all the valency electrons per atom in it (*viz.*, 6 per atom, since electron atom ratio of MoS_2 is 6) bounded by planes $(\bar{2}11,0)$ and (000,6), which are planes of large energy discontinuity. It is a hexagonal prism with its axis along 'c' of height $\frac{6}{c}$ and side $\frac{2}{a\sqrt{3}}$. The diamagnetism is then to be attributed to the few electrons that overlap beyond this *Zone*, *i.e.* whose Fermi surfaces extend slightly beyond the planes of energy discontinuity.[7] Since the planes bounding the Brillouin *Zone* are planes of large energy discontinuity causing the overlap to be very small and since these planes occur symmetrically with respect to the origin, it is possible to regard the overlapping electrons as forming a number of ellipsoidal distribution in k-space having the origin still at the centre.

From the nature of the Brillouin Zone and in view of the small value of α_3, it is evident that the band width in the direction of the principal axis is very

small *i.e.* electrons can take up all permitted values k_x. Similarly it is evident that along directions in the basal plane very high values for either α_1 or α_2 is not possible. Thus the electrons along the basal plane behave as though they are free, whereas at right angles to the plane their motion is highly restricted.

EXPLANATION FOR THE ABSENCE OF THE SPIN-PARAMAGNETISM

Normally the spin paramagnetism should predominate over the diamagnetism of the free electrons except when $\frac{1}{3}\alpha_1\alpha_2$ is very great causing the spin paramagnetism to be insignificant. But according to our previous findings $\alpha_1=\alpha_2=1$. However an explanation of the type offered by Ganguli and Krishnan (1941) in the case of graphite is also applicable here for explaining the absence of any spin of the free electrons at ordinary temperatures. It can be assumed that each of the energy levels are either occupied by an electron pair of opposite spins or not occupied at all. In the occupied levels the energy of the coupling between the spin-moments may be assumed to be large in comparison with the energy corresponding to temperatures ordinarily attainable. Thus the spins remain balanced for ordinary temperatures. If in addition, the occupied energy levels are so closely spaced that they may be regarded as almost continuous, the energy of distribution will be practically the same as when the spin-spin coupling is absent. The coupling will not therefore affect the diamagnetism of the electron gas and the temperature variation of the diamagnetism will be in accordance with the theory postulated for the purpose. When the temperature of the electron gas is very high—so high that the corresponding energy attains a value sufficient to cause the dissociation of the components of a pair of electrons with opposite spins. Above this temperature the diamagnetism is expected to be completely masked by the spin-paramagnetism.

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